Original Research Article

Chemical Desulphurization of Coal using KOH as Oxidizing Agent in the Presence of Deep Eutectic Solvent

Akasha Saleem[1], Nasir Abbas[2], Dur-e-Shehwaar[1], Tayyaba Shabir[3], Noor Hassan[4*], Muhammad Munawwar[5]

[1]Department of Chemistry, University of Agriculture Faisalabad 38000 Pakistan
[2]Department of Chemistry, Ghazi University, Dera Ghazi Khan 32200 Pakistan
[3]Department of Chemistry, Women University Multan 66000 Pakistan
[4]School of Chemistry and Chemical Engineering, Beijing Institute of Technology100081, P.R. China
[5]Department of Sericulture, Silk Grainage center Cart road, 47140 Murree, Pakistan

Abstract

Coal is a great source of energy gifted by the nature. Main hazard in the use of coal is the production of sulphur oxides, sulphur dioxides, and nitrogen oxides which affect the climate severely. To protect environment from these hazardous oxides of sulphur, clean coal technology is being introduced and applied all over the world. Various desulphurization methods such as chemical, physical or biological have been used. In this study oxidative desulfurization using highly efficient deep eutectic solvent (DES) was carried out by ultra-sonication method. Choline chloride and ethylene glycol in 1: 2 ratios were used to prepare DES. Oxidative desulfurization process was utilized to treat coal samples using KOH as an oxidant. Oxidative desulphurization (of organic/inorganic sulphur forms) of coal was achieved by using deep eutectic solvent. ASTM methods were used to estimate different forms of sulphur in coal. The Fourier Transform Infrared spectroscopy (FTIR) was used to estimate the amount of sulphur removed from three different coal samples.
Keywords: Desulphurization, deep eutectic solvent, ultra-sonication, ASTM methods.

1. INTRODUCTION

The process of removal of sulphur from coal is known as desulfurization of coal. Desulfurization of coal is a chemical process that is used to remove sulphur from any material. It includes removal of sulphur or sulphur compounds from any mixture. It includes removal of sulphur from oils, coals and flue gas. Desulfurization is required in natural gas.

The sulphur present in coal, oil can convert into many forms like hydrogen sulphide, carbonyl sulphide, sulphur oxides or mercaptans. High level of sulphur in these mixtures causes problems in proper exertion of coal. The emission of sulphur compounds can combine with water vapours. This is a major cause of acid rain. The combustion of coal releases sulphur dioxide and nitrogen oxides which are a main cause of acid rain. These are considered as pollutant causing air pollution. So, it is very important to remove to sulphur. Sulphur has harmful effects on the exertion of coal like burning and coke making. Much of air pollution is begin by the direct combustion of coal. Removal of

sulphur is very important issue in coal industry. Desulfurization can be performed by; physical, chemical and biological methods. Physical methods can be utilized to remove inorganic sulphur. These may include forth floatation. Magnetic separation, washing, oil agglomeration. Desulfurization can also be done by in bed desulfurization and flue gas desulfurization [1].

Desulfurization may include variation: Hydro desulfurization, extractive desulfurization, oxidative desulfurization, bio desulfurization, desulfurization by alkylation and using super critical fluid. Although desulfurization can be performed by physical and biological methods, but chemical methods is considered as the most efficient method. Sulphur species particularly hydrogen sulphide gas produces toxicity for the environment so chemical desulfurization process can be applied to remove it. Chemical desulfurization can reduce the amount of sulphur dioxide that is released into the atmosphere during the process of utilization of coal it is basically a hydrometallurgical

process. Chemical oxidation can be used for removal of organic sulphur from low rank coal.

The process of desulfurization can also be performed using nitric acid. It helps in the rapid elimination of pyritic sulphur and sulphates. The removal of organic sulphur can be done by chemical methods but the conditions for these reactions are severe so the use of microwave radiations from the removal of sulphur from coal is more convenient [2].

These are the alternative technologies which are also being used now a day. Microbial desulfurization of coal is also known. This is done using microorganisms. For this purpose, mostly chemolithoautotrophic bacteria like T. thiooxidans and T. ferroxidase can be used. Coal pyrolysis can be used as well. Chemical desulfurization can also be done by using various oxidizing agents like hydrogen peroxide, ferric sulphate. These are effective in eliminating pyritic sulphur, and ash, sulphate sulphur. The use of liquid chlorine for the desulfurization of high sulphur coal has also expressed. Hydrogen peroxide solutions can also be used for oxidative desulfurization. Electrolysis can also be performed for desulfurization [3].

Sulphur is present in coal as organic, inorganic and pyrite sulphur forms. Sulphur contents in coal different in size but is mostly ranges of 0.5%- 5% of total contents. Coal with less than 1% sulphur is classified as low sulphur coal while 1 to 3% is called medium sulphur coal and having more than 3% sulphur is classified as higher sulphur coal. Sulphate and sulphide are forms of inorganic sulphur. Organic sulphur in coal exists in the form of sulphides, disulphides, thiophenes, cyclic sulphides, thiols and aliphatic sulphides (Mishra *et al*., 2014). Calcium and iron sulphates are two common forms of sulphate present in coal. Pyritic sulphate is present in form of FeS_2 in coal. Pyritic sulphur is determining from the amount of iron removed by HNO_3. Electron probe microanalysis, scanning electron microscopy, X-ray's analysis, and transmission electron, are methods used for sulphur contents determination. Chemical methods are used to elimination of organic sulphur from coal [4].

Desulfurization and removal of mineral matter are very vital for sustainable commercial use of low-grade coals. High sulphur content can be reduced by desulfurization. Desulfurization can be used to enhance coal quality and it can be used for multipurpose such as coke. When coke having sulphur, content is used in steel industry. It reduced the plasticity and make them brittle. Many methods are used for removal of sulphur such as physical, flotation, chemical, biotechnology and microbial methods. Physical method can be used for removal of pyrite and sulphate. Other effective methods are also oxydesulfurization and alkali desulfurization used for removal of sulphur from high coal [5].

Sulphur contents in coal are converted into sulphur oxides during combustion process and can cause acid rain. It's a major environmental problem. Thus, desulphurization of coal is a crucial step to reduce sulphur oxides, sulphur dioxides emissions and their respective environmental problems. The common method of sulphur removal from coal is catalytic hydrodesulphurization. This method is used for efficient removal of mercaptans, thioethers, and disulphides but cannot be used for removal of aromatic organo sulphur compounds such as dibenzothiophene DBT. In liquid fuel the oxidation of refractory organosulfur compound is coupled with effective liquid. Immiscible solvents (i.e., oxidative desulfurization) are used for subtraction of the oxidized sulphur compounds in liquid.

Deep eutectic solvents are ionic liquid type and are consistent to each other because low melting point properties are same. Ionic liquid is well-defined as a solution with melting point below the boiling point of water [6]. Ionic liquids are known by several different names like neoteric, ionic fluids [7], molten salts and designer solvents. Inorganic anions and organic cations are composition of ionic liquid [8]. To be liquid at room temperature, the cation should preferably be unsymmetrical [9] that is, the alkyl groups should be different. Polarity and hydrophilicity (mix easily with solution) hydrophobicity of ionic liquids can be tuned by suitable combination of cation and anion [10]. It is this property of ionic liquids which has earned them the accolade "designer solvents" [11]. As a solvent, ionic liquids have found applications in several reactions has been reviewed extensively the applications of ionic liquids. Ionic liquid is used as a catalytic phase in several organometallic reactions [12].

It was reported that these have ability to remove sulphur compounds which is exhibited by tetrafluoroborate $[BF_4]^-$ based ionic liquids, but because of their instability with the formation of $[HF]^-$ in the presence of water and their relatively high price, their application as large scale extracting agents is not ideal. Depending on its acidic property, hydrogen-bonding ability and in its place of a simple attention of environmental protection, the authors choose the non-fluorinated $[HSO_4]^-$ as the anion of the measuring ionic liquids primarily. Coal structure could be simply swelled due to the strong hydrogen bonding ability of $[HSO_4]^-$, which can help sulfur-containing structures in coal to dissolve in IL-H_2O_2 solutions. Another reason is that to improve the oxidizability of H_2O_2 each of these ionic liquids with $[HSO_4]^-$ could deliver an acidic medium Additionally, acidic ionic liquids with $[HSO_4]^-$ have competent capability of desulfurization substitute as extractants as well as catalysts according to the described researches on oil desulfurization, Because of it is low price, not strongly corrosive, non-polluting, and commercially accessibility, H_2O_2 is an ideal oxidant [13].

Formation of deep eutectic solvent is done using quaternary ammonium salt and hydrogen bond donor HBD. Extraction of organosulfur compound occurs due to having interaction between deep eutectic solvents and liquid fuel. Deep eutectic solvent act as green solvent. By involving DES quantum calculation is attained. This is done to describe the thermodynamics, charge behaviour, intermolecular interactions linked with the application of organosulfur removal. Between aromatic sulphur compounds ASCs (benzothiophene and dibenzothiophene) with chlorine chloride and hydrogen bond donor, a weak monovalent interaction exists. However, in between ASC and chloride ion due to maintenance of conventional hydrogen bond of initial DES no interaction present. For further Spectroscopic and proximate analysis techniques will be used for further characterization [14].

In this research work, ultrasound energy in water and alkali (KOH solutions) along with the eutectic solvent will be used for removal of various forms of sulphur from high sulphur coal samples.

2. MATERIAL AND METHODS
This research study was designed to observe the oxidative desulfurization of coal using KOH in deep eutectic solvent. This solvent based on choline chloride and ethylene glycol 1:2 ratios. The schematic study of research work is discussed below:

2.1 Samples of coal
Sample 1: Sample Kanz-Ul-Aswad Collieries, Khushab 143
Sample 2: Sample Kanz-Ul-Aswad Collieries, Khushab 144
Sample 3: Agha Mining Contractors 527

Table 2.1: List of chemicals used

Sr. No	Chemicals and reagents	Percentage purity	Formula	Company Name
1.	Choline Chloride	99%	ChCl	DAEJUNG
2.	Ammonium hydroxide	25 to 30%	NH_4OH	Merck
3.	Magnesium Oxide	97%	MgO	Merck
4.	Sodium Carbonate	99.9%	Na_2Co_3	DAEJUNG
5.	Barium Chloride	99.9%	$BaCl_2$	DAEJUNG
6.	Hydrochloric Acid	37%	HCl	Merck
7.	Distilled Water		d H_2O	Lab
8.	Nitric Acid	65%	HNO_3	Merck
9.	Potassium hydro Oxide	85%	KOH	DAEJUNG
10.	Bromine	99%	Br_2	UNI-CHEM

Table 2.2: List of instruments used

Instruments	Manufacture	model	Specifications
Electronic Balance Digital	KD-NBCD-300		o.2g-300g
Analytical Balance Digital	G & G	JJ224BC	0.0001g-220g
Muffle Furnace	Snol Omron	E5CC	Up to 1100 ^{0}C
Mechanical Stirrer	SCILOGEX	OS20-S	50 to 2200rpm
Sonicator bath	Universal ultrasonic cleaner	(DSA50-SK2-25L)	40KHz

2.1.1 Description of apparatus used
The apparatus used in the present study includes conical flask (250 ml, 500 ml), flat bottom flask (250 ml, 500 ml) volumetric flask, measuring cylinder (10 ml, 100 ml, 250ml), ceramics crucibles, pipette (10 ml), sucker, beakers (100ml, 250ml, 500ml), magnets, stain-less steel spatula, Whatman filter paper no.42, reagent bottle (with screw cap), aluminum foil, funnel, glass rods, petri plates, burette, pH papers.

2.2 Preparation of solution of reagents
2.2.1 Barium chloride ($BaCl_2$) solution (100g/1000ml)
Weighed 100g of $BaCl_2$ was added into a volumetric flask of 1000ml volume. The volume of flask then distilled water was taken to the mark.

2.2.2 Sodium carbonate ($NaCO_3$) saturated solution (w/v)
Measured 22g of $NaCO_3$ was added in 100ml flask and the volume was completed 100 ml solution.

2.2.3 Indicator Methyl orange solution (0.02g/100ml)
0.02g methyl orange added in flask and now the volume of the flask was made up to 100ml with deionized water.

2.2.4 1Molar Potassium Hydroxide KOH Solution (w/v)
56g of KOH precisely weighted was added in volumetric flask with volume completed 1000 ml using distilled water.

2.2.5 Grinding, Sieving

To meet the experimental necessities, coal is shaped into a decreased size while completed crushing and creating fines particles is not recommended. The samples are required to break into little size particles claiming that these are gathered in huge lumps. The samples were isolated 27 into grindable size and after that in stainless steel mill samples were more crushed. The Octagon Sieves (OCT – Digital 4527-01) was utilized to disperse coal into various particle size as indicated by investigational necessities. The granulated coal was then disconnected from particle size of 50 µm, 200 µm, 400 µm, 600 µm, 750 µm, 800 µm and 950 µm respectively.

2.3 Proximate analysis

One of the massive analysis is proximate analysis that indicate that percentage of ash content, volatile matter, moisture contents and fixed carbon. A proximate examination includes the following:

- After coal combustion the remaining material is called ash content which usually contain aluminum (Al) magnesium (Mg), silica (SiO_2), iron oxide (Fe_xO_Y) and calcium (Ca). It is thus necessary to pure the coal retention the true objective to reduce its mineral contents.
- Volatile matter (V.M) results from the organic as well as inorganic matter in coal. In a simple approach coal is burning in air. On burning, organic matters produce from oil, tars, hydrogen, hydrocarbon gases and oxides of carbon also. Fixed inorganic matter can distribute un-ignitable volatiles, that, if appear in enough measures, impact the operation of coal.
- Moisture contents are present in holes of coal widely. This is main impact on the energy assessment of coal. Because a rise in moisture content reduces the coal estimation calorific value [15].
- This estimation of fixed carbon (F.C) is difference method. In this method, the difference of moisture, volatile and ash contents subtracted from 100. It is not an analysis method that's why the faults happening in other analysis may apparent in the fixed carbon. During the coal samples comparison, fixed carbon value is very beneficial.

2.4 Sulphur in coal

Sulphur is principally related to coal in three unique structures: sulphate minerals, sulphide minerals, and organic composites. Though, proportionate extent of these structure depends upon the kind and nature of coal. For the most part calcium sulphate ($CaSO_4$) and iron sulphate ($FeSO_4$) related to sulphate sulphur (SO_4^{2-}) in coal. Pyrite (FeS_2) dominates in sulphide mineral group. Thiols, thiophens, sulphides, disulphides and cyclic sulphides exists in coal in form of organic sulphur which is explicitly bound to organic matter of coal.

It has been signified that another sort of sulphur which is familiar as secondary sulphur in coal that is neither just organic nor basically pyritic is reported recently. Carbon combustion with expended sulphur content speaks to a notable division of total general generation of anthropogenic sulfur dioxide is harmful, dangerous and an inactive environmental pollutant that causes acid rain. They have compelled different nations to apply firm measures to decrease SO_2 releases. Thus prior to its utilization as a fuel, it is mandatory to remove out the sulfur from coal.

2.5 Sulphate

The mineral sulphate assessed in coal don't regularly compromise an enormous amount of mineral matter exist in unoxidized fresh coal samples. After the mined, the oxides of iron disulphides fast oxidize through the reports of formations hydrates like $FeSO_4.XH_2O$ are present. In hard coal, barium sulphate and gypsum are found. After the weathering process of pyrite, different sulphate is formed which are hydrated types of ferrous sulphate just as ferric.

2.6 Sulphide

Pyrite mineral is the most abundant then marcasite. Both are the main sulphides mineral present in coal and are the dimorphs forms they have same chemical formula but different crystal structure. Generally, marcasite is orthorhombic while pyrite exists in isometric form. Both largely contribute to the total amount of sulfur present in coal and they are removed easily. Corrosion, boiler tube fouling, and pollution due to discharge of gases like sulfur dioxide, when the coal is burned are caused by these sulphur minerals.

2.7 Organic sulfur

To the main structure of coal like benzothiophene, dibenzothiophene. organic sulfur is attached chemically. A little bit of thermal stability shown by this sulfur.

2.8 Calorific value (CV)

Based on its calorific value, American Society of Testing of Materials (ASTM) classified the low ranked coal because it contains the low calorific value. Enthalpy of combustion or specific energy (SE) are the names sometimes referred to the calorific value. When a material burned, the quality of heat energy per unit weight of that material released. The measurement of this released energy is called calorific value (CV). In between the atoms the bond energies are present which are associated with this property and from the determination of the basic configuration it can be calculated with higher accuracy.

2.9 Preparation of deep eutectic solvents

Preparation of deep eutectic solvents were prepared by two methods. First was heating and second was vacuum evaporating method. The DES contain

choline chloride and ethylene glycol was prepared in   lab is shown in

Figure 3.1:

Figure 3.1: Preparation of deep eutectic solvent in laboratory

1. **Heating Method**

In this method, a known amount of water was added to prepare deep eutectic solvent. The mixture with two components (ChCl: ethylene glycol) in 1:2 and calculate quantity of water was added in a caped conical flask along with a magnetic stirrer. The flask was then placed in a water bath over a hot plate at 60 ^{0}C for almost two hours until a clear solution of deep eutectic solvent was obtained.

2. **Vacuum evaporating method:** To prepare deep eutectic solvent, the mixture components were dissolved with water in a rotary evaporator with a temperature of 50 ^{o}C for evaporation. Desiccation of the obtained liquid was done with silica gel until a constant mass was attained.

2.10 Desulfurization process

Desulfurization of coal was done by oxidation process with oxidizing agents KOH in deep eutectic solvent. For the oxidation purpose, ultrasonic method was utilized to treat all these samples (527, 144, 143). Following samples with different ratio were prepared:
1. Coal: KOH (1M KOH)
2. Coal: water
3. Coal: KOH: DES (ethylene glycol: ChCl)

In this treatment 1, 20 g of raw coal sample along with 100ml water and KOH (1M each) was added in a 250 ml conical flask. In treatment 2, 9g samples of coal along with 100ml of distilled water was added in

flask. In treatment 3, 4g samples of coal along with 10ml DES (ethylene glycol: ChCl) and 0.56g KOH was taken in the volumetric flask. Oxygen bomb calorimeter was used to calculate the calorific value. Approximately 1g of coal sample is used to calculate the calorific value. To determine ash contents from coal, thermos gravimetric analyzed is used. Sulphur analyzer is used to estimate total sulfur contents [16].

2.11 Ash contents

As per the standard test method, ASTM D-3174, the inorganic ash content is estimated by burning precisely to analysis of coke as well as coal at around 700-750 °C temperature for 4 hours.

2.12 Moisture contents

The determination of moisture contents is done by calculating the weight loss of sample (expressed in the form of sample weight percentage) which has been passed through the micro sieves of 60-mesh size (250 μm). According to ASTM D-3173 standard test method, under controlled conditions in an inert environment at 107 ± 30 ^{o}C for about 1h, 1g of sample is maintained for the estimation of moisture form the sample of coke and coal.

2.13 Volatile matter

A pre-weighed crucible with a height of 30- 35 mm, a diameter of 26- 35 mm and a capacity of 10- 20 ml having a closed fitting cover was used for the determination of volatile matter. Accurately weighed 1g

of coal sample was added in the crucible. The crucible was then allowed to stand in the chamber of furnace at a specified height. The place where the crucible could stand must have the temperature sustained at 950 $^{\circ}$C $\pm$ 20 $^{\circ}$C. At that point volatile matter is freed rapidly. It must be guarantee that the cap is firmly secured to prevent against discharge of air. In the furnace, give heating temperature for 7-8 minutes, it is then displaced and cooled. At the point when crucible is cold, it must be adjusted. The percentage of volatile matter is equivalent to the difference between weight reduction rate and moisture percentage [17].

2.14 Fixed carbon

After estimation of volatile matter, ash contents, moisture contents, fixed carbon is the remaining contents to be determined. After volatile matter removal, fixed carbon is actually a solid inflammable estimation material in coal. The one of the qualities used to decide the effectiveness of coal burning plants is fixed carbon. It is a strong material as fuel remaining subsequent to expelling the temperamental substances in the coal. For this reason, it is additionally utilized as a sign of coke execution in a cooking procedure. The fixed carbon esteems, revised for the dryness of the mineral substances, are utilized as parameters of the standard indexing of the ASTM D388 coal categorizing system [18].

2.15 Calorific value

The energy discharged upon burning is of basic interest to coal makers and clients. The calorific value, on a predefined basis, is one of the more significant parameters utilized in the coal classification. It most significant parameter in coal ignition. It is the amount of heat discharged when coal is burned per unit mass of substance.

The broadest technique for the estimation of coal calorific value is the utilization of bomb calorimeter; specific strategies are chosen to utilize these calorimeters so as to check the gross calorific value of coal just as coke in ASTM standard test method for D-5865. As per these strategies, an oxygen bomb was taken, submerged in water with weighed sample that is ignited in a pot encased by a coat. The temperature of the coat and water temperature of calorimeter must be same in an adiabatic calorimetric framework[19]. The temperature increments in calorimeter are balanced in an isothermal calorimeter framework for the heat gain or lose through the estimation from nearby coat.

2.16 Eschka method for total sulphur determination

Eschka mixture in Eschka method consist of magnesium oxide (MgO) and sodium carbonate (Na$_2$CO$_3$) in the 2:1 proportion. Blend them carefully on a coated paper before adding in crucible and utilized 3 grams of Eschka mixture for 1 g of coal. To avoid the rapid elimination of volatile matter, crucibles are warmed and put in a corner-to-corner position on a tripod stand at exceptionally on low fire thus the sulphur product from ignition process can be prevented from the complete absorption. Warmth the crucibles for around thirty minutes. Put the crucibles into muffle furnace and gradually increase the temperature about 800 °C for 1 hour. Keep up this temperature until all the black particles disappeared [20].

Take away the crucible from furnace and empty the substance into a beaker of 200 ml capacity and digest it with 100 ml of hot distilled water for half hour and shake irregularly. Pour the solution by filter paper holding however much insoluble material in the beaker as could reasonably be expected. Remove the crucibles from furnace and empty the mixture into a container of 200 ml limit. Digest the mixture with 100 ml of hot deionized water for half hour and shake randomly during the specified time. Pour the solution by using filter paper over a funnel holding anyway much insoluble material in the measuring glassware as could as possible.

The un-dissolved matter was washed with warm water in a glassware. After couple of washes, move the insoluble material through filtration and wash few times by warm water and mix up the substance appropriately. Filter the solution (up to 250 ml) and include methyl orange neutral solution as an indicator with sodium hydroxide or sodium carbonate (if acidic solution) and in this manner HCl (approximately 1 ml HCl is added to the filtered solution if it is basic). The pH paper was used to check the pH of the solution. Warmth to the point of bubbling and blend 10 ml or to a more BaCl$_2$ solution. BaCl$_2$ should be in excess. In the process BaCl$_2$ solution if in excess amount (more than 10ml), the sample weight reduction to 0.5 gram occurs and repeats digestion and inflammation process. Warmth for 15 minutes and let stay for nearly 2 hours or preferably overnight at below the boiling point so that precipitates of BaSO$_4$ obtained.

Weighed out the filter paper and then filter the solution containing precipitates. Whatman no. 42 filter paper was preferably used to filter the solution and then wash it with warm water even silver nitrate drop may produce and formed opalescence (milky brightness) when is added.

Total sulphur in coal sample by Eschka method estimated as:
Percentage of sample for analysis = (PW $\times$ 13.71) /C
Molecular weight of BaSO$_4$ = 233.38 g/ mol
Molecular weight of sulphur = 32 g/ mol
233.38 g of BaSO$_4$ contain sulphur = 32 g
1g of BaSO$_4$ contain sulphur = = 0.1371
Percentage of sulphur in 1 g of BaSO$_4$ = 0.1371 $\times$ 100 = 13.71
PW = weight of BaSO$_4$ precipitates (in g)
C = weight pf coal sample taken (in g)

Total sulphur – Sulphur removed = Extracted sulphur
% removal of total sulphur after treatment = $\times 100$

2.17 Sulphate sulphur

For the sulphate estimations, 2-5 g of the sample was blended with HCI (one volume of concentrated HCl and three volumes of distilled water) and reaction was permitted to stand for 30 minutes. The apparatus used in sulfate sulfur estimation is shown in

Figure 2.2:

Figure 2.2: Sulphate sulphur estimation in laboratory

The carbon which is stayed undissolved is isolated out with filtration and washed for the pyrite sulphur estimation (it can spoil or discarded, and another sample of pyrite sulphur may be utilized, bromine water (at its saturated state) filter was blended to oxidize different types of sulphur in the sulphate ion and the ferric ions into ferric. Bromine water in excess is removed by heating to the boiling temperature; the iron was isolated by precipitation with NH_3 (in excess amount) and filtered [21].

The precipitate ought to be utilized to determine non pyritic iron if there a fresh carbon sample was used for iron pyrites calculation. By precipitation with the $BaCl_2$ and $BaSO_4$ the sulphate sulphur was then isolated and determined gravimetrically.

Calculations to determine percentage sulphate sulphur are as follows:
Percentage of sample for analysis = (PW × 13.71) /C
Molecular weight of $BaSO_4$ = 233.38 g/ mol
Molecular weight of sulphur = 32 g/ mol
233.38 g of $BaSO_4$ contain sulphur = 32 g
1g of $BaSO_4$ contain sulphur = = 0.1371
Percentage of sulphur in 1 g of $BaSO_4$ = 0.1371 × 100 = 13.71
PW = weight of $BaSO_4$ precipitates (in g)
C = weight pf coal sample taken (in g)
Total sulphur – Sulphur removed = Extracted sulphur
% removal of sulphate sulphur after treatment = $\times 100$

2.18 Referee method for pyrite sulphur estimation

In the reference method for pyrite sulphur estimation, 1 g of coal sample was taken in 250 ml of flat bottom flask and covered it with 80 ml of dilute HNO_3 and permitted to stand with periodic shanking for around 2 hours at room temperature (25 °C). Discarded the residue after filtration and several washes of coal sample with chilled water. This sort of treatment oxidized iron into Fe (III) and inorganic sulphur into sulphate. After oxidation, the reaction mixture is filtered, and the filtrate could be utilized for estimation of iron by Atomic Absorption Spectroscopy (AAS) or by titration method. If iron in pyrite sulphur is to be estimated by the previously mentioned method (AAS), no extra work is done in the filtration, with the exception of dilution of the filtrate to a volume proper for the sample test. On the other hand, if titration method is utilized to estimate iron, 30 % H_2O_2 is added in the filtrate to expel any carbon discoloration [22]. The iron was then precipitated out, separated and washed out with distilled water. At that point the precipitates were blended with HCI and determined by titration with iron $KMnO_4$, or $K_2Cr_2O_7$.

Calculations:

Percentage concentration of pyrite sulphur can be estimated as follows;
Stoichiometric ratio of sulphur to iron (S: Fe) in iron disulphide (FeS_2) = 1.148

2.19 Difference method for organic sulphur estimation

The organic sulphur amount present in coal sample can be determined effectively by difference method that is subtracting the pyritic and sulphate sulphur from total sulphur. It can be explained as:
Organic sulphur = Total sulphur – (Sulphate sulphur + Pyrite sulphur)

Percentage removal of sulphur

Following calculation was done to check the percentage removal of sulphur from all three coal samples (527, 143 and 144):
% Removal = (A) × 100

A = Sulphur present before treatment
A = Sulphur present after treatment

2 RESULTS AND DISCUSSION

The above Table 1 contains the properties of deep eutectic solvents including their ratio, viscosity, conductivity, refractive index and density as well. The proximate analysis includes sulfur and ash content, volatile matter, fixed carbon, total moisture and calorific values. The effect of DESs on the organic sulfur, sulfate sulfur and pyritic sulfur of coal samples are given in tables. Data shows the significant removal of sulfur from coal by DESs. This result shows the removal of sulfur from pyritic sulfur is 63-78%, sulfate sulfur is 26-45%, organic sulfur removal is 45-64% and total sulfur removal is 52-63% using oxidation treatments. As the coal samples are crushed to particle size of 0.25mm diameter for running the experiment.

Table 1: Properties of deep eutectic solvents

SOLVENTS	Ratio	Viscosity/cP	Conductivity/ mS cm^{-1}	Refractive index	Density/ g cm^{-3}
Choline chloride: Ethylene glycol	1:2	632	1.05	1.469	1.24

Table 2: Composition of coal samples

Coal types	Sample Agha Mining Contractors 527 (Sample 1)	Sample Kanz-Ul-Aswad Collieries, Khushab 143 (Sample 2)	Sample Kanz-Ul-Aswad Collieries, Khushab 144 (Sample 3)
Total Sulphur (%)	3.38	5.98	4.68
Total Moisture (%)	14.02	2.56	3.02
Ash (%)	4.65	25.75	22.10
Volatiles	43.36	35.98	39.13
Fixed Carbon	37.70	35.71	35.75
Gross Calorific Value (kcal/kg)	5,962	4,967	5,491

3.1 Oxydesulfurization of coal by DESs

The coal sample 1 before treatment contains 5.98%, 2.3%, 0.98% and 2.7% of total sulfur, pyritic sulfur, sulphate sulfur and organic sulfur respectively. Treatment 1 of KOH as oxidizing agent and (DESs) ChCl: Ethylene Glycol with coal were removed 3.39 %, 0.89 %, 0.31% and 1.30% of total, pyritic, sulphate and organic sulfur respectively under reflux condition of 1 hour that shows 55% removal of total sulfur, 65% removal of pyritic sulfur, 36% removal of sulphate sulfur and 45% removal of organic sulfur.

As well as treatment 2 of KOH with coal were removed 2.54%, 1.24%, 0.46% and 1.15% of total, pyritic, sulphate and organic sulfur respectively under reflux condition that shows 42% removal of total sulfur, 54 % removal of pyritic sulfur, 46 % removal of sulphate sulfur and 42% removal of organic sulfur [23].

Similarly, treatment 3 of H_2O with coal was removed 2.27 %, 0.75 %, 0.25% and 1.01 % of total, pyritic, sulphate and organic sulphur respectively under reflux condition that shows 38 % removal of total sulphur, 32 % removal of pyritic sulphur, 26% removal of sulphate sulphur and 37 % removal of organic sulphur.

While the second part of table displays the percentage removal of total sulphur content in coal. It shows that after using oxydesulfurization ultra sonication method of sample 1 with KOH + DES (choline chloride: ethylene glycol) total sulphur is reduced to 48% while without DES using KOH and water separately total sulphur removal is 44% and 39% respectively. The treatments with KOH have more percentage removal than the treatments with water. But KOH lonely does not show better desulphurization while with DES the desulphurization rate of total sulphur enhanced greatly. DES act to increase the

desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasonic bath with high frequency which have potential to desulphurize coal along with oxidant and DES [24].

While the second part of table displays the percentage removal of total sulphur content in coal. It shows that after using oxydesulfurization ultrasonicator method of sample 2 with KOH + DES (choline chloride: ethylene glycol) total sulphur is reduced to 55% while without DES using KOH and water distinctly total sulphur removal is only 50 % and 43% correspondingly

show in Table-2. The treatments with KOH have more percentage removal than the treatments with water. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of total sulphur enhanced greatly DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasonic energy (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES.

Table 3: % removal of TS from samples

Treatments	Sample 1	Sample 2	Sample 3
ChCl: KOH+ Ethylene glycol	48%	55 %	51%
KOH	44 %	50 %	48%
Water	39 %	43 %	41%

The Table 3 displays the percentage removal of total sulphur content in all three coal samples. It shows that after using oxydesulfurization method of sample 3 with KOH + DES (choline chloride: ethylene glycol) total sulphur is reduced to 51 %. while without DES using and water separately total sulphur removal is only 48 % and 41 % respectively. The treatments with KOH have more percentage removal than the treatments with water because water remove only mineral matter

and bond between sulphur and carbon is not break but KOH lonely does not show better desulphurization while with DES the desulphurization rate of total sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency occurs which have potential to breakage of bond in coal along with oxidant and DES.

Table 4: % removal of PS from samples

Treatments	Sample 1	Sample 2	Sample 3
ChCl: KOH+ Ethylene glycol	61 %	62 %	42 %
KOH	54 %	56 %	34 %
Water	32 %	34 %	26 %

In Table 4 For sample 1 using ultrasound energy method, pyrite sulphur is removed 61 % when treated with KOH + choline chloride: ethylene glycol (DES). On the other hand, 54 % and 32 % of pyrite sulphur is removed using KOH and water distinctly without deep eutectic solvent treatment. The treatments with KOH have more percentage removal than the treatments with water. But KOH lonely does not show better desulphurization while with DES the desulphurization rate of pyritic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In sonication method the high frequency (40 kHz) occurs which have potential to breakage of particles of coal along with oxidant and DES.

For sample 2 using ultrasound energy (40 kHz) method, pyrite sulphur is removed 62 % when treated with KOH + choline chloride: ethylene glycol (DES). On the other hand, 56 % and 34 % of pyrite sulphur is removed using KOH and water separately without deep eutectic solvent treatment. The treatments with KOH

have more percentage removal than the treatments with water. But KOH lonely does not show better desulphurization while with DES the desulphurization rate of pyritic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occur which have potential to desulphurize coal along with oxidant and DES [24].

For sample 3 using ultrasound energy with high frequency (40 kHz) method, pyrite sulphur is removed 42 % when treated with KOH + choline chloride: ethylene glycol (DES). On the other hand, 34 % and 26 % of pyrite sulphur is removed using KOH and water separately without deep eutectic solvent treatment. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But KOH lonely does not show better desulphurization while with DES the desulphurization

rate of pyritic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In

ultrasound energy, the high frequency occurs which have potential to desulphurize coal along with oxidant and DES.

Table 5: % removal of SS from samples

Treatments	Sample 1	Sample 2	Sample 3
ChCl: KOH+ Ethylene glycol	68 %	63 %	70 %
KOH	46 %	50 %	47 %
Water	26 %	27 %	34 %

The removal of sulphate sulphur is 68 % with KOH and choline chloride: ethylene glycol in sample 1 ultrasonicator method. Only 46% and 26% of organic sulphur is removed using KOH and water respectively without the deep eutectic solvent as shown in Table-5. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of sulphate sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES.

The removal of sulphate sulphur is 63% with KOH and choline chloride: ethylene glycol in sample 2 ultrasonicator method. Only 50% and 27% of organic sulphur is removed using KOH and water respectively without the deep eutectic solvent as shown in table. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better

desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of sulphate sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurization coal along with oxidant and DES [25].

The removal of sulphate sulphur is 70 % with KOH and choline chloride: ethylene glycol in sample 3 ultrasonicator method. Only 47 % and 34 % of organic sulphur is removed using KOH and water respectively without the deep eutectic solvent as shown in table. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxide while with DES the desulphurization rate of sulphate sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES.

Table 6: % removal of OS from samples

Treatments	Sample 1	Sample 2	Sample 3
ChCl: KOH+ Ethylene glycol	39%	33 %	36 %
KOH	38%	29 %	26 %
Water	33%	25 %	33 %

Using ultrasonicator method, when coal sample 1 is treated with KOH and choline chloride: ethylene glycol solution, organic sulphur is removed 39 % of the total sulphur present in coal. In contrast, organic sulphur removal is 38 % and 33 % using KOH and water respectively without deep eutectic solvent as shown in Table-6. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong

oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of organic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES.Using ultrasonicator method, when coal sample 2 is treated with KOH and choline chloride: ethylene glycol solution, organic sulphur is removed 33 % of the total sulphur present in coal. In contrast, organic sulphur removal is 29 % and

25 % using KOH and water respectively without deep eutectic solvent. The treatments with KOH have more percentage removal than the treatments with water because water is only removing mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of organic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES [26].

Using ultrasonicator method, when coal sample 3 is treated with KOH and choline chloride: ethylene glycol solution, organic sulphur is removed 36 % of the total sulphur present in coal. In contrast,

organic sulphur removal is 26 % and 33 % using KOH and water respectively without deep eutectic solvent. The treatments with KOH have more percentage removal than the treatments with water because water is only removed mineral matter (ash content) and does not break bond between sulphur and carbon. But ultrasound energy with KOH lonely does show better desulphurization because KOH is a strong oxidizing agent to oxidized sulphur into sulphates, sulphone and sulphoxides while with DES the desulphurization rate of organic sulphur enhanced greatly. DES act to increase the desulphurization rate as well as it also acts as extractant for sulphur in all coal samples. In ultrasound energy, the high frequency (40 kHz) occurs which have potential to desulphurize coal along with oxidant and DES.

The results of all forms of sulphur described in all above tables are shown in graphs of Figure 3.1. Figure 3.2 and Figure 3.3.
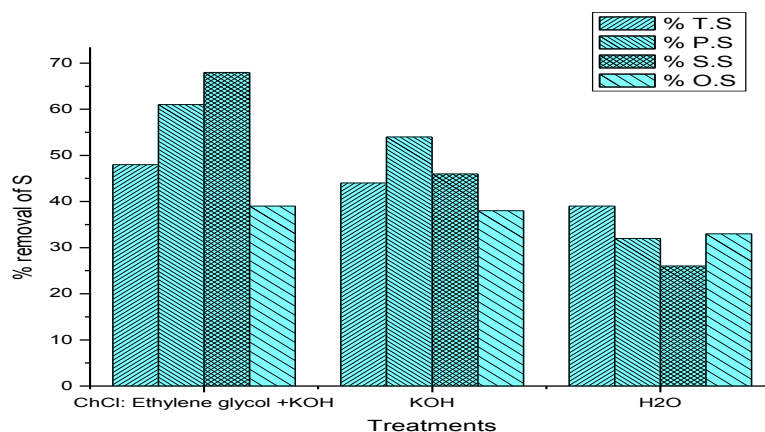

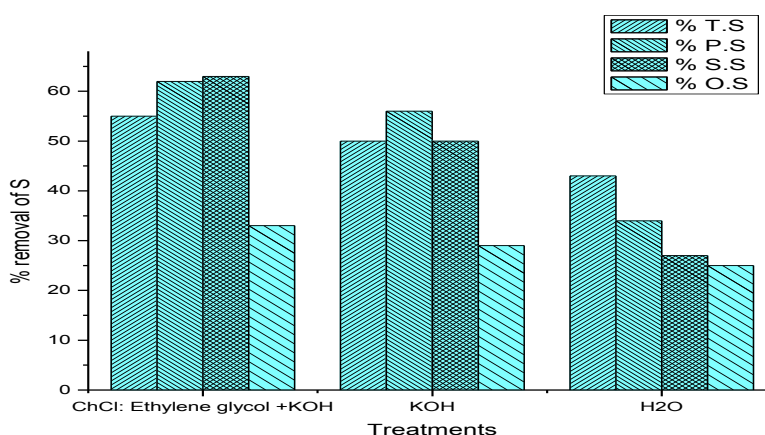**Figure 3.1: % Removal of total sulfur from coal sample 1**

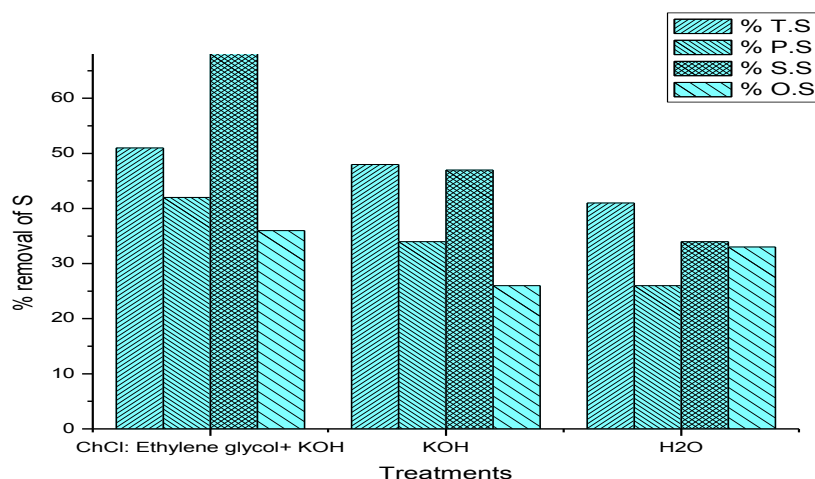**Figure 3.2: % Removal of total sulphur from coal sample 2**

Figure 3.3: % Removal of total sulphur from coal sample 3

Table 7: Calorific values of coal samples treated and untreated

Coal samples	Calorific value (k.cal/kg)
143- glycerol	3,930
143- untreated coal	**4,976**
144-glycerol	4,007
144- untreated coal	**5,491**
527-glycerol	4,975
527- untreated coal	**5,962**

A fixed percentage of heat is released in the ignition process after the burning of coal. All coal has certain calorific and low fixed carbon value shown above Table-7, accordingly to ASTM D-388. The calorific value of sample 1 is 4,976 kcal/kg, sample 2 having 5,496 kcal/kg and sample 3 having 5,962 kcal/kg in high volatile bituminous coal. (addtmd-388).

3.1 Proximate analysis

The present research has been accepted on coal sample obtain from PCSIR Laboratory Complex Lahore Pakistan. The total moisture content, volatile matter (VM), and ash results are generally between the key factors utilized for calculating the value of coal. These are observed by number of tests that are recognized as proximate analysis. Current study ash content, fixed carbon, volatile matter and total moisture content, were evaluated according to ASTM methods (ASTM) [27].

For sample 1, ash content was higher comparatively low for sample 2 and extremely small extent for sample 3 as 25.74 %, 22.12 % and 4.64 % correspondingly. Coal ash is a remaining metal oxide subsequent to the cooking of coal. It is the mineral which remains after sulfur, carbon, oxygen and water, together with clays excluded through coal burning.

The analysis of coal samples was approved on conventional basis. The volatile matter (VM) in coal samples 1, 2, 3 such as 35.97 %, 39.12 % and 43.64 %, respectively. The volatile matter rises certainly with reducing the quality of coal. Coal V.M direct to the carbon constituent, with the exclusion of moisture content, that is released at a high temperature in the unavailability of air [28]. In sample 1, less quantity of moisture content is detected that was 2.56 % of the total weight while sample 2 contain around 3.02 % and sample 3 contains 14.02 % of total weight. Calorific value significantly affected by moisture content. More than, the moisture of coal decreases and the calorific value in the latent heat of vaporization increases [29].

After the combustion of coal, a fixed percentage of heat is released in the combustion process. All coal has low fixed carbon and definite calorific value accordingly to ASTM D-388. The calorific value of sample 1 is 4,976 kcal/kg, sample 2 having 5,496 kcal/kg and sample 3 having 5,962 kcal/kg in high volatile bituminous coal.

Fourier Transform Infrared Spectroscopy
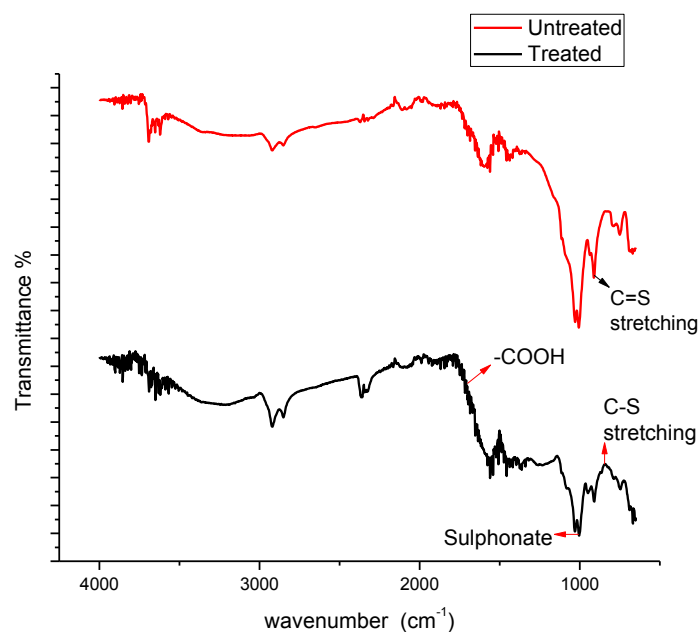
Figure 3.4: FTIR spectra of sample 1
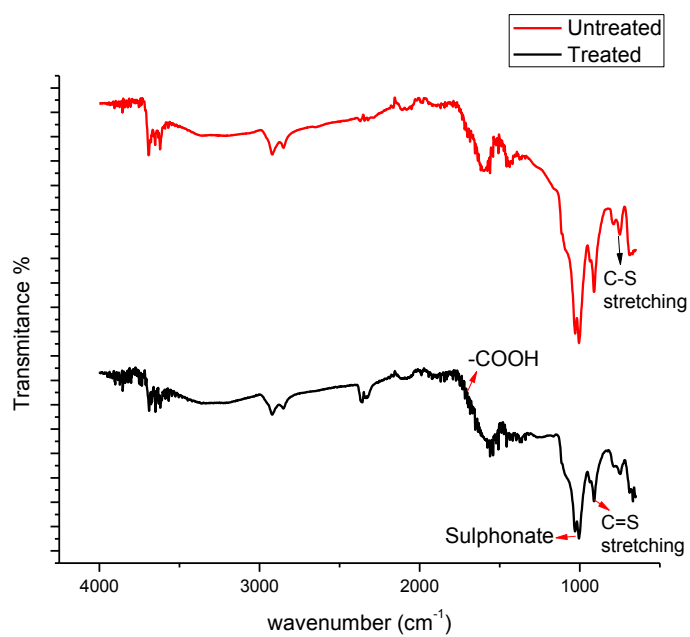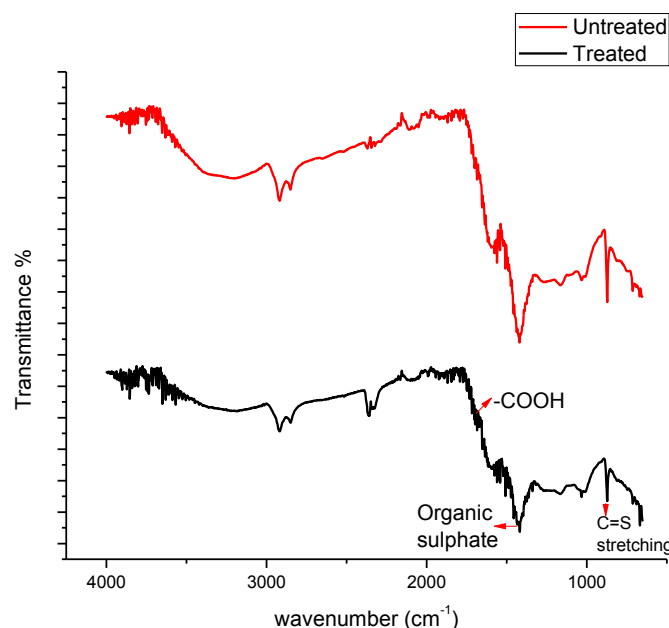

Figure 3.5: FTIR spectra of sample 2

Figure 3.6: FTIR spectra of sample 3

Figure 3.4, Figure and Figure 6 shows FTIR peaks of all three samples. When FTIR spectra of treated and untreated coal samples are compared, it shows no significant changes except the relative intensity of some absorption bands. For sample 1, the peak at 756 cm^{-1} shows the C-S linkage that diminishes for treated samples. Moreover, the peak at 1450 cm^{-1} in raw coal is due to organic sulphates.

The peak near 3600 cm^{-1} is the major hydrophilic oxygen functional group which indicates that hydrophilicity of the oxidized coal may decrease with treatment of KOH. The sharp peak at 1028 cm^{-1} is due to the sulfonate salts which decreases after the treatment. Similarly, the sharp absorption peak at 872 cm^{-1} in sample 3 is attributed due to the C=S stretching vibration.

CONCLUSION

In this Research work, our purpose was to eliminate or reduce the sulfur content from coal samples. Three types of coal samples were occupied from PCSIR laboratory Complex Lahore, Pakistan having different sulfur content. The determination of inorganic sulfur, sulfate sulfur, organic sulfur and total sulfur of coal samples were confirmed. Fixed carbon, Proximate analysis containing volatile matter and ash content as well as calorific value were also verified. Higher sulfur content is found in coal sample 1 of sub-bituminous coal. Samples were characterized by calorific values and calorific value of coal was determined by bomb calorimeter.

Desulfurization of coal was carried out by ultrasonic treatment with oxidizing agent such as KOH. Deep eutectic solvents were used also adding choline

chloride: ethylene glycol (1:2). The sulfur removal by this technique was originated to be 50-61%. The inorganic sulfur removal that is sulfate and pyritic sulfur was originated to be removed about 56-80% due to the adding of deep eutectic solvents followed by ultrasonic solution. Higher chemical desulfurization is attained under reflux condition being around 58% and 66% for total sulfur and organic sulfur, respectively.

The calorific values for sample 1, 2 and 3 were found by solvent choline chloride: ethylene glycol and KOH 5,209 Kcal/Kg, 5,702 Kcal/Kg and 4,879 Kcal/Kg respectively. Similarly, calorific values with oxidizing agent KOH was found 5,195 Kcal/Kg, 5,697 Kcal/Kg and 4,852 Kcal/Kg correspondingly for sample 1, 2 and 3. With water for sample 1, 2 and 3, calorific values were found 5,231 Kcal/Kg, 5,719 Kcal/Kg and 4,925 Kcal/Kg respectively with ultrasonic treatment.

Using ASTM standard test methods, proximate analysis of coal samples was performed. It was found that coal sample 1 contains moisture content of about 2.58% of total weight, while sample 2 contains 3.02% of moisture and sample 3 contains 14.02% of moisture content. It was observed that higher the moisture content lower is the calorific value which indicates low rank coal. Similarly, with the increase in volatile matter calorific value is decreased accordingly. The volatile matter for coal samples 1, 2 and 3 were found 43.63%, 39.13% and 35.98% respectively. Volatile matter is the coal constituent apart from moisture content that is released without air at elevated temperature. Ash content in sample 1 is 25.75%, in sample 2 22.10% and 4.65% in sample 3. It is the mass remaining of non-metal oxides as a deposit in the coal sample after combustion.

For further analysis, Fourier transform infrared spectroscopy was used on coal samples before and after the treatment with deep eutectic solvents. The FTIR gives the peaks of sulfur containing compounds and the formation products like sulfoxides as well as sulfonate.

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